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Natural $^{1}H^{1}H$ spins decoupling in water in the presence of ^{17}O

Vily Marius Cimpoiaşu
University of Craiova, Craiova, Romania

Romulus Ion Scorei
University of Craiova, Craiova, Romania

Radu Popa*
Portland State University, Portland, OR, 97201, USA

Abstract

The nuclear spin and quadrupole of ^{17}O influence the ortho (O) and para (P) organization of proton pairs in water at intra-molecular (i.e. within the $H_2^{17}O$ molecule), and inter-molecular level (i.e. water molecules adjacent to $H_2^{17}O$). We used fourier transform infrared spectroscopy ($FTIR$) to analyze $O:P$ ratios in $H_2^{16}O$ and $H_2^{17}O$ ($OPR16$ and $OPR17$), and time domain 1H nuclear magnetic resonance ($TD-1HNMR$) to analyze changes in the abundance of $P-$coupling relative to changes in the concentration of $H_2^{17}O$. $FTIR$ results showed that $OPR16 \approx OPR17 \approx 3$. The combined $1HNMR$ signal of intra-molecular and inter-molecular coupling was $71.64\% O+P$.

1 Introduction

In water, the strongly coupled $^{1}H^{1}H$ nuclear spin pairs can be ortho- (O) coupled (triplet; three states with total spin $I=1$) or para- (P) coupled (singlet; one state with $I=0$). At room temperature the $O:P$ ratio of $H_2^{16}O$ ($OPR16$) is about $3:1$ [1]-[2]. External factors can introduce changes in this organization [3], which may take the form of altered OPR values or changes in the overall abundance of $O+P$ organization ($\%O+P$). Typical examples of such external factors include nuclear spins [4] and electromagnetic fields [5]-[7]. Changes in $O\&P$ organization can in turn influence chemical reactivity [8], more important for processes involving weak chemical bonds. It was reported earlier that alterations in proton exchange reactivity in aqueous solutions are correlated with the concentration of $H_2^{17}O$ ($[H_2^{17}O]$), an effect attributed to the ^{17}O nucleus [9]-[11]. The ^{17}O isotope has non-zero nuclear spin and a large nuclear electric quadrupole moment. Thus, it can alter the $^{1}H^{1}H$ spin:spin organization of $H_2^{17}O$ or that of neighboring water molecules. The exact nature of these alterations, their mechanism and extent are very difficult to predict in complex three spin systems such as $^{1}H^{1}H^{17}O$, or in mixtures of water isotopomers ($H_2^{16}O$ and $H_2^{17}O$), and require experimental verification as well.

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*Corresponding Author: *rpopa@pdx.edu*

Sources for changes in the ${}^1H^1H$ spin:spin organization in the presence of $H_2^{17}O$.

In this section we start with analyzing the energy of ${}^1H^1H$ interaction via four spin:spin coupling mechanisms. Then, we compare the difference in chemical shift between protons with the magnitude of the ${}^1H^1H$ J coupling. This comparison helps evaluate whether $O\&P$ organization occurs in the ${}^1H^1H^{17}O$ system, and whether $H_2^{17}O$ can influence $O\&P$ organization in neighboring water molecules as well.

Strongly coupled ${}^1H^1H$ systems. For two spins to be strongly coupled two conditions need be fulfilled: (1) the two spins have to have the same nature; and (2) the two spins have to be magnetically equivalent or the difference in chemical shift frequencies has to be smaller than their spin:spin coupling energy. Figure 1 shows an example of a system of two water molecules, $H_2^{17}O$ and $H_2^{16}O$, bound via an H-bond and containing two ${}^1H^1H$ nuclear spin pairs. Each of these two pairs can exhibit strong $O\&P$ coupling.

Weakly coupled ${}^1H^1H$ systems. The ${}^1H^1H$-spin system is said to be weakly coupled if the general condition is satisfied: $|\omega_1 - \omega_2| >> 1/2 \left|\omega_{12}^B\right|$; where: $\omega_{12}^B = 2\pi J_{12} - d_{12}$. In isotropic liquids, the secular dipole-dipole coupling d_{12} disappears and the general condition shown above becomes: $|\omega_1 - \omega_2| >> \pi J_{12}$. In conditions of asymmetry between the two ${}^1H$'s, the heteronuclear ${}^1H^1H^{17}O$ spins system is almost always weakly coupled, in the sense shown above. In the presence of an external magnetic field 24 energy level states exist. A simple way to derive this number is by stepwise analysis. Each ${}^1H$ spin (having two states $-1/2$ and $1/2$) can be analyzed as it interacts separately with the spin of ${}^{17}O$ ($I = -5/2, -3/2, -1/2, 1/2, 3/2$ and $5/2$). In a ${}^{17}O$:${}^1H$ group twelve states are generated. Their combination with the second ${}^1H$ spin will result in 24 states. In these 24 states, and if not strong ${}^1H^1H$ coupling occurs, the three spins are weakly coupled and all ${}^1H$ protons are visible by ${}^1HNMR$ signal amplitude. In the three spins system ${}^1H^1H^{17}O$ the ${}^1H^1H$ pairs have the possibility to be weak coupled or strongly coupled. The proportion between these two states depends on the spatial and interaction asymmetry of the $H_2^{17}O$ molecule.

Mechanisms of nuclear spin:spin coupling. Four mechanisms by which the ${}^{17}O$ nucleus can intervene in the organization of ${}^1H^1H$ spin systems are summarized next.

- Direct (dipole-dipole) nuclear spin coupling between the ${}^{17}O$ spin and a ${}^1H$ spin from the same molecule (i.e., intra-molecular short range interaction). The full form of the direct dipole-dipole interaction between two spins is given in the spin Hamiltonian ($\widehat{H}_{jk}^{DD,full}$) by the term: $\widehat{H}_{jk}^{DD,full} = b_{jk}(3(\hat{I}_j \cdot e_{jk})(\hat{I}_k \cdot e_{jk}) - \hat{I}_j \cdot \hat{I}_k)$; where:$b_{jk} = -\frac{\mu_0}{4\pi} \cdot \frac{\gamma_j \gamma_k \hbar}{r_{jk}^3}$; $\hat{I}_j$ and $\hat{I}_k$ = the two nuclear spins;γ_j and $\gamma_k$are the gyromagnetic ratios of the spins; r_{jk} is the distance between the two spins; and $\mu_0 = 4\pi \cdot 10^{-7} Hm^{-1}$ is the magnetic constant [12]. Table 1 gives the energies associated with short range intra-molecular interactions in water molecules, based on the distances from Figure 1 and under the most favorable orientation of spins and nuclei.

- Long range direct nuclear spin coupling between the ${}^{17}O$ spin from $H_2^{17}O$ and a ${}^1H$ spin from another water molecule across an H-bond (see Figure 1). The energy of this inter-molecular interaction is given in Table 1.

- Indirect J-coupling between spins through one or two chemical bonds within the $H_2^{17}O$ molecule. The full form of the intra-molecular J-coupling between two nuclear spins of the same molecule is $\widehat{H}_{jk}^{J,full} = 2\pi \cdot \hat{I}_j \cdot J_{jk} \cdot \hat{I}_k$; where: J_{jk} is the J-coupling tensor [12] . The energy of interaction between spins through J-coupling, assuming water as an isotropic fluid, is given in Table 1.

- Electric quadrupole coupling between ${}^{17}O$ and ${}^1H$. For this estimation we used the first order quadrupolar Hamiltonian $\hat{H}_Q^{(1)} = \omega_Q^{(1)} \frac{1}{6}(3\hat{I}_z^2 - I(I+1)\hat{I})$; where:$\omega_Q^{(1)} = \frac{3eQ\ \bar{V}_{ZZ}}{2I(2I-1)\hbar}$ is the first order quadrupolar coupling; $\bar{V}_{ZZ}$ is the average electric field gradient component over molecular motion; Q is the electric quadrupole moment of the nucleus; and Î is the spin quantum number [12] . The Nuclear Quadruple Coupling Constant ($NQCC$) $\frac{e^2Q\bar{V}_{ZZ}}{h}$ monitors the electric field gradient $\bar{V}_{ZZ}$ in the nucleus site. The usual $NQCC$ value is in the $10^6 - 10^9 Hz$ ($6.6 \cdot 10^{-28} - 6.6 \cdot 10^{-25} J$) range, comparable to $9MHz$ (˜$10^{-26}J$) from NHF_2 (a highly asymmetric environment) and much smaller than a few kHz (˜$10^{-30}J$) seen in NH_4^+, which is a symmetric environment [13] . The ^{17}O Quadrupole Coupling Constant ($OQCC$) for the isotropic motion of water molecule was estimated to be about $8.1MHz$ [14] , or $7.9 \pm 0.3MHz$ [15],[16] , substantially smaller than the ab initio value of $8.9 \pm 0.3MHz$ was found earlier [17],[18] and calculated for non-isotropic motion. Table 1 gives the energy of the electric quadrupole coupling using $OQCC = 9MHz$.

Mechanism of asymmetry; The source of chemical shift difference between hydrogen protons.

Inside the ^{17}O-water molecule, or when $H_2^{17}O$ binds another molecule via a H bond, at least two situations can render the two ^1H atoms non-equivalent: (i) varying distance between the ^{17}O nucleus and the two ^1H nuclei within the $H_2^{17}O$ molecule caused by the v_3 asymmetric stretch; and (ii) $J^{17}O^1H$ –coupling if ^{17}O across one H bond (a case of asymmetric exchange).

Case (i) Within the three spins system $^1H^1H^{17}O$, calculating the $^1H^1H$ differences in chemical shift frequencies depends on the asymmetry described above. A necessary condition for the modification of the $\%O + P$ is the breaking of the symmetry between the two hydrogen atoms. Even in the presence of a magnetic field this symmetry breaking is achieved by the dipolar interaction with a third spin (^{17}O). Asymmetry exists in water molecules due to thermal oscillations, creating protons with dissimilar magnetic environments. For a v_3 asymmetric stretch of the OH bond varying between 70% to 140% relative to the equilibrium bond length of $0.09578nm$ [19] , the energy difference between two protons, because of difference in chemical shift in the presence of ^{17}O is: $E_{|\omega 1 - \omega 2|} = 1.631 \cdot 10^{-28} J$, calculated from the difference in E^{DD} $|\omega 1 - \omega 2| = 1.55 \cdot 10^6 rad$. As shown above the J-coupling between the two ^1H nuclei in water is 9.4 Hz and thus $\pi J_{12} = 29 rad$. In the case of asymmetric long range intermolecular interaction between ^{17}O and neighboring $H_2^{16}O$ molecule (see Figure 1) the chemical shift difference is even larger (see Table 1). In this case, the asymmetry is mediated by the correlation time.

Another source of asymmetry is the electric quadrupole interaction. In this state, the E_Q energy appears because of the electric field gradient of the ^{17}O site. The key question is whether this interaction is symmetric or asymmetric. Some authors assumed that in liquid phase water molecules execute isotropic reorientation [15],[16] , with $OQCC 7.9 \pm 0.3MHz$, while others assumed that ^{17}O-water molecule has non-isotropic reorientation [20] . In the later case, electric quadrupole interaction may appear.

In other scenarios, if ^{17}O-water molecule is bonded to substrate (i.e., cannot rotate freely), the quadrupolar interaction becomes highly anisotropic and $E_Q \neq 0$, because of the nonzero electric field gradient of the ^{17}O site, generated mostly by the v_3 asymmetric stretch [19] .

Case (ii) The interaction between the ^{17}O spin and ^1H spin pair can be exemplified during chemical exchange. During proton exchange between water molecules and the surrounding solution, the water molecules dissociate into OH^- and H^+. Briefly, the $^1H^1H$ spins become separated and the O and P states disappear. During this time the ^{17}O nuclear spin interacts with the singular ^1H nuclear spin from the ^{17}OH- group (i.e., intramolecular ^{17}O:^1H spin:spin interaction).

For the above we deduce that the ^{17}O nucleus should partly decouple proton pairs from water molecules at both intra-molecular and inter-molecular level. Because it is controlled by many factors, the exact magnitude of this effect remains difficult to compute, making experimental validation desirable. We made measurements in solutions of water isotopomers ($H_2^{16}O$; $H_2^{17}O$ and $H_2^{18}O$) using $FTIR$ spectroscopy and $TD-{}^1HNMR$. $FTIR$ can analyze OPR values [21] , while ^1HNMR spectroscopy can help study spin:spin coupling because its signal intensity is proportional to the magnitude of those ^1H nuclei population having non-zero magnetic moments [22],[23],[24] . Combined, these two methods help analyze the effect of $H_2^{17}O$ on $^1H^1H$ decoupling in water.

2 Materials and Methods

Principle and materials and methods for $FTIR$ measurements

Rotational and vibrational (i.e., rovibrational) transitions in water are observable by infrared (IR) spectroscopy and can be linked with specific O or P couplings [25],[26],[27] . Limitations of IR when used to analyze the OPR of water include: OPR differences between gas phase and liquid phase, low peak resolution in liquid phase, the peaks of liquid phase rovibrational transitions not being as well described as in gas phase, and uncertainty about whether IR peak amplitude ratios measure spin:spin coupling as well. Earlier analyses of O and P in water were made in near IR [25] and far IR [26],[27] . In gas phase $FTIR$ measurements peaks are very sharp and $OPR16$, $OPR17$ and $OPR18$ can be determined by collective analysis of a large number of transition peaks [1]. In liquid phase IR peak resolution and peak definition is poor and only a few single $O => O$ and $P => P$ ($OO\&PP$) line pair transitions were identified that show $OPR \approx 3$ [2] . We used $FTIR$ to analyze absorption peaks corresponding to quantum state rovibrational transitions from $(v_1v_2v_3)JK_aK_c$ to $(v_1\prime v_2\prime v_3\prime)J\prime K_a\prime K_c\prime$. The rule of thumb is that $v_3+K_a+K_c$ is odd for O and even for P, obviously only should strong $^1H^1H$ coupling occur [21] . Gas phase $FTIR$ spectra for water isotopomers were obtained from $HITRAN08$ [28] . The liquid phase IR measurements were made with a Thermo Electron Nicolete spectrometer. We analyzed the $400-4000cm^{-1}$ range, at 20^oC and 384 scans per sample. The contribution of each line to the spectrum was considered Lorentzian, with the half-width at half-height equal to the instrument function of our spectrometer ($0.2cm^{-1}$). We analyzed water mixtures from sources with different proportions of isotopomers ($H_2^{16}O$, $H_2^{17}O$ and $H_2^{18}O$). We used ultra pure water with natural $19mM$ $H_2^{17}O$ and $111mM$ $H_2^{18}O$ concentrations, and water enriched with $5.9M$ $H_2^{17}O$ and $20.9M$ $H_2^{18}O$ from Spectra Stable Isotopes (MD). ^{17}O-rich water containing $4.8M$ $H_2^{16}O$, $50.3M$ $H_2^{17}O$ and $0.4M$ $H_2^{18}O$ was obtained from Isotec (CA). After identifying the peaks corresponding to each $OO\&PP$ transition pair we used peak amplitude values to calculate OPR values according to Mumma et al., 1987 [1] . We analyzed OPR values for $H_2^{16}O$, $H_2^{17}O$ and $H_2^{18}O$ using collective analysis (i.e. all $OO\&PP$ pairs within a wavelength range and all $OO\&PP$ pairs within single vibrational bands) and single $OO\&PP$ pair analysis.

Principle and materials and methods for NMR measurements

The principle of measuring changes in the abundance of spins by NMR (in the case of H_2 and water O and P organization as well) is based on this technique's capability to distinguish magnetic properties of target nuclei. When spins are strongly coupled, the P state is NMR-silent ($\mu_P \approx 0$), which is contrary to the O state ($\mu_O \approx 5.586\mu N$) or to weakly coupled and uncoupled states ($\mu \approx 2.792\mu N$), [22],[24],[29] . Earlier methods to analyze P/O conversions based on high resolution NMR [24] , do not work in the presence of $H_2^{17}O$ due to the broad width of the NMR line caused by the scalar relaxation of protons with ^{17}O, which has a large nuclear quadrupole Q of about 0.26 barns [30] . In this case low resolution $TD -^1 HNMR$ is necessary. Because $P-$coupled protons do not participate to the ^1HNMR signal amplitude, this measurement is proportional with the sum between the weakly coupled ^1H spins, the $O-$coupled ^1H spins and the uncoupled ^1H spins. Thus, if the pH and OPR are known, TD-^1HNMR results can be used to analyze changes in the abundance of strongly coupled $^1H^1H$ spin pairs. We studied the effect of $[H_2^{17}O]$ on changes in TD-^1HNMR signal amplitude in pure water. To ascertain which isotope, ^{17}O or ^{18}O, produces the largest change in the ^1HNMR signal we used water sources with different $^{17}O/^{18}O$ isotopic ratios: $H_2^{16}O$ with $5.9M$ $H_2^{17}O$ and $20.9M$ $H_2^{18}O$ from Spectra Stable Isotopes (MD), and water with $22.8M$ $H_2^{17}O$ and $23.9M$ $H_2^{18}O$ from Rotem GmbH (Germany). For dilutions, we used $dH2O$ with environmental concentrations of ^{17}O and ^{18}O ($19mM$ and $111mM$ respectively). The pH of all water samples was ˜7, determined after NMR measurements. A $25MHz$ spectrometer ($B_o = 0.589T$) Aremi $TD - LRP$ equipped with an audio filter with $1MHz$ bandwidth and quadrature phase sensitive detector was used to acquire spectra at $298 \pm 0.2K$. For precise amplitude measurements total spin relaxation is needed, which was obtained by applying a classic $CPMG$ sequence [31],[32] with short inter-pulse delays ($400\mu s$). This sequence restricted the chemical exchange from influencing the spin-spin relaxation [10] . We used $200 \pm 2\mu L$ volumes of water and did 71 independent $TD -^1 HNMR$ readings of four mixtures of water isotopomers containing $0.019M, 0.588M, 5.88M$ and $22.83M$ $H_2^{17}O$ and $0.111M, 2.087M, 20.868M$ and $23.865M$ $H_2^{18}O$ respectively. Amplitude readings were corrected relative to the isotope mass content and to the spectrometer's electronic gain, using a single mineral oil reference measured before and after each sample. All water samples and the reference were thermo-stabilized for ˜12 hours at 25^oC before being measured. For each value of mass concentration we made sufficient measurements to obtain a steady general trend and good statistical separation between the various concentrations.

3 Results

$FTIR$ **results**

Collective analysis of all gas phase $FTIR$ bands in the $2.26 - 24,991.00cm^{-1}$ range gave $OPR16 = 2.999$, $OPR17 = 3.0014$ and $OPR18 = 3.0003$. This analysis was based on $36,400$ lines for $H_2^{16}O$, $6,979$ lines for $H_2^{17}O$ and $9,737$ lines for $H_2^{18}O$. In liquid phase, the $FTIR$ peaks were broader and more variable in width than in gas phase; and only a small fraction of the gas-phase $HITRAN$ peaks could be unambiguously identified in the liquid phase spectrograms as well. Some wavelength areas were crowded with numerous overlapping peaks of the various water isotopomers, making peak deconvolution impossible. This limitation prohibited collective analysis of all lines within a wavelength range. Comparison of single vibrational bands of gas phase $FTIR$ results gave variable OPR values among the different bands and consistently larger $OPR17$ than $OPR16$. Again, because of numerous overlapping peaks, single band OPR analysis was also not possible in liquid phase $FTIR$ of mixed solutions of water isotopomers. Earlier workers recommended analyzing single $FTIR$ OO&PP pairs that at equilibrium show $OPR \approx 3$ [2],[25],[27],[33] . Still, we found that OPR values varied significantly among various $OO\&PP$ pairs. For example, in gas phase $FTIR$ the $OO\&PP$ transition pair (010)634 to (000)523 (OO) & (010)533 to (000)422 (PP) gives $OPR16 = 1.75$, while the pair (010)441 to (000)330 (OO) & (010)542 to (000)431 (PP) gives $OPR16 = 5.014$. We compared

OPR values based on $OO\&PP$ homologous pairs between different water isotopomers and between gas phase and liquid phase water. If $FTIR$ analysis is an accurate means to determine OPR values, our results show significant OPR differences between gas phase $H_2^{16}O$ and liquid phase $H_2^{16}O$, between gas phase $H_2^{17}O$ and liquid phase $H_2^{17}O$, and also between $H_2^{16}O$ and $H_2^{17}O$ in both gas and liquid phase. Very few examples of $OO\&PP$ pairs were found that allow simultaneously comparing "liquid phase OPRs" with "gas phase OPRs", while at the same time comparing $OPR16$ with $OPR17$. One such example is the $OO\&PP$ pair (010)432 to (000)321 (OO) & (010)331 to (000)220 (PP), which gave $OPR16 = 2.024$ and $OPR17 = 2.019$ in gas phase, and $OPR16 = 1.25$ and $OPR17 = 2.7$ in liquid phase. Because $H_2^{17}O$ molecules may also influence the OPR of neighboring $H_2^{16}O$ molecules, we also analyzed changes in $OPR16$ in mixtures of liquid water with different $[H_2^{17}O]$ $(0.019M, 5.9M$ and $50.3M)$. Based on nine $OO\&PP$ transition pairs, shown in Table 3, we found no sizable effect of $H_2^{17}O$ on $OPR16$ from solution.

$TD -^1 HNMR$ **results**

In NMR the relationship between changes in the abundance of ${}^1H^1H$ P-coupling and signal intensity is linear. Multiple regression analysis of 71 independent $TD -^1 HNMR$ readings of water mixtures containing various concentrations of $H_2^{17}O$ and $H_2^{18}O$ led to the following relationship.

$Signal\ intensity = 2447.4 + 4.35 \cdot [H_2^{17}O] - 0.21 \cdot [H_2^{18}O]$

The R_2 between intensity averages and $[H_2^{17}O]$ was 0.997, indicating that most of the variation in signal intensity was due to changes in $H_2^{17}O$ and not $H_2^{18}O$. For $OPR16 = OPR18$ the $OPR17$ contribution to signal intensity was approximated to be:

$Signal\ intensity = 2446.49 + 4.14 \cdot [H_2^{17}O]$

In Figure 2 the Y intercept represents the contribution of all ${}^1H$ nuclei, minus the P-coupled ${}^1H$ nuclei, to the signal intensity in pure $H_2^{16}O$. We attribute the increase in signal intensity in the presence of $H_2^{17}O$ to higher abundance of non-P-coupled protons. Uncoupled ${}^1H$ spins of free protons in solution (H^+) or from OH^- groups could not have significantly influence these measurements because at pH 7 very few water molecules are dissociated and because the changes in signal amplitude we found showed $> 10\%$ difference between $H_2^{16}O$ and $H_2^{17}O$. The pH drift during the measurements was not significant (results not shown).

Table 1. Summary of energies associated with four mechanisms of spin:spin coupling involving ${}^1H$ and ${}^{17}O$ nuclei from water molecules.

	Direct intra-molecular E^{DD}	Direct inter-molecular E^{DD}	Indirect intra-molecular	Electric quadrupole
	short range interactions	long range interactions	E^{iso} J-coupling	coupling E_Q
${}^{17}O$-${}^1H$	$6.19 \cdot 10^{-29}J$	$3.53 \cdot 10^{-29}J$	$4.688 \cdot 10^{-31}J$	$5.9 \cdot 10^{-27}J$
${}^1H$-${}^1H$	$2.32 \cdot 10^{-29}J$	–	$0.978 \cdot 10^{-32}J$	–

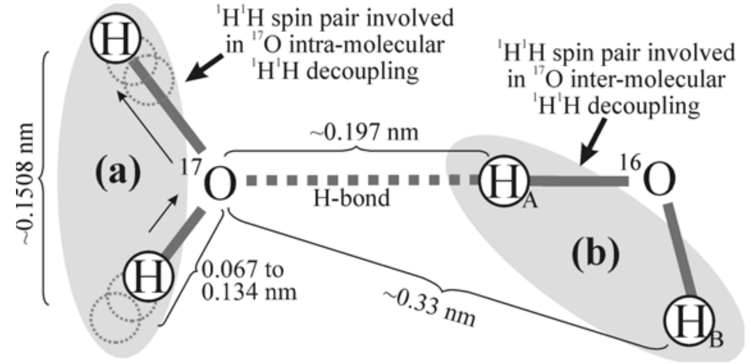

Figure 1: System of two water molecules ($H_2^{17}O$ and $H_2^{16}O$) bound through an H-bond and containing two $^1H^1H$ nuclear spin pairs (a) and (b). Both these pairs can show weak and strong $O\&P$ coupling. This coupling may be influenced by the ^{17}O nucleus at the intra-molecular level (a) or inter-molecular level (b). The v_3 asymmetric stretch of water, used to analyze the intra-molecular $^1H^1H$ decoupling, is shown in (a). The dissimilar distance between the ^{17}O nucleus and the H_A and H_B nuclei ($^{17}O - H_A \neq {}^{17}O - H_B$) is the basis for analyzing the ^{17}O inter-molecular $^1H^1H$ decoupling.

Table 2. Energy difference between protons, which is used to compare the tendency of the ^{17}O nucleus to alter the $O + P$ organization in $^1H^1H$ proton pairs at the intra-molecular level and inter-molecular level (see. 1). The $^1H^1H$ coupling has ordering ffects and increases the probability for $O + P$ strong coupling ($\%O + P$), while the chemical shift difference between ^1H and ^1H increases disorder, i.e., decreases the probability for $O + P$ organization (i.e. increases $^1H^1H$ decoupling).

	Intra-molecular effect ($H_2^{17}O$)	Inter-molecular effect ($H_2^{16}O$)
$^1H^1H$ coupling	$9.78 \cdot 10^{-33}J$	$9.78 \cdot 10^{-33}J$
Chemical shift difference	$9.40 \cdot 10^{-32}J$	$5.55 \cdot 10^{-30}J$

Table 3. List of nine distinguishable single $FTIR\ OO\&PP$ pairs in mixtures of water isotopomers, and the type of $^1H^1H$ spin coupling they are associated with.

Transition from:	Type of coupling	Transition to:	Type of coupling
(010)212 to (000)303	OO	(010)111 to (000)202	PP
(010)423 to (000)532	OO	(010)322 to (000)431	PP
(010)532 to (000)643	OO	(010)431 to (000)542	PP
(010)321 to (000)212	OO	(010)220 to (000)111	PP
(010)414 to (000)505	OO	(010)313 to (000)404	PP
(010)101 to (000)110	OO	(010)202 to (000)211	PP
(010)110 to (000)101	OO	(010)211 to (000)202	PP
(010)716 to (000)725	OO	(010)615 to (000)624	PP
(010)212 to (000)321	OO	(010)111 to (000)220	PP

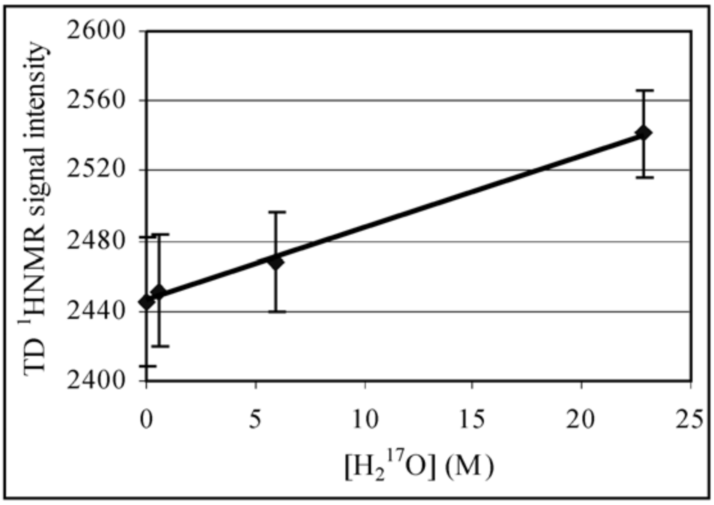

Figure 2: Evolution of $TD -^1 HNMR$ signal amplitude relative to $[H_2^{17}O]$. The data points are averages of multiple readings of water with different concentrations of $H_2^{17}O$ (16 for $0.019M$; 21 for $0.588M$; 15 for $5.88M$ and 18 for $22.83M$).

4 Conclusions

The ^{17}O nucleus may induce decoupling of $^1H^1H$ spin pairs in the $H_2^{17}O$ molecule itself, but also in other adjacent water molecules (within one H bond distance). We propose that part of the loss in strong $^1H^1H$ coupling can be attributed to direct coupling between the ^{17}O and ^1H nuclear spins via short range and long range interactions. On theoretical grounds we predict that the level of $^1H^1H$ decoupling ($\%O + P$) is higher in $H_2^{17}O$ than in adjacent $H_2^{16}O$ molecules. Calculating the exact differences in $\%O + P$ between $H_2^{17}O$ and $H_2^{16}O$, and the overall level of $^1H^1H$ decoupling remains difficult. Collective $FTIR$ analyses of OPR values are difficult in liquid phase mixtures of water isotopomers. Single $FTIR$ pairs (in both liquid and gas phase) are too variable to measure the OPR, though they may remain useful in some applications, such as studying trends in ΔOPR under various experimental conditions. Collective gas phase $FTIR$ analyses showed that the water isotopomers $H_2^{16}O$, $H_2^{17}O$ and $H_2^{18}O$ have very similar OPRs (≈3). Most changes in ^1HNMR signal amplitude of water were likely due to changes in $H_2^{17}O$, rather than $H_2^{18}O$. The effect of the ^{17}O nucleus on the bulk $H_2^{16}O$ solution was not significant, but this does not eliminate the possibility for $H_2^{17}O$ to decouple $^1H^1H$ spin pairs from $H_2^{16}O$ molecules that are bound to $H_2^{17}O$ via H bonds. ^1HNMR signal amplitude could not discriminate between intra-molecular and inter-molecular decoupling caused by ^{17}O. For $OPR = 3$, 100 % disorganization of the $^1H^1H$ spin pair systems should increase the ^1HNMR signal intensity by ≈33 %. Our results show lower abundance of P in the presence of $H_2^{17}O$ from 25 % to 17.91 %. $OPR16 = OPR17 = 3$, this corresponds with a level of $^1H^1H$ decoupling of about 28.4%. The effect of ^{17}O on the strong $^1H^1H$ spin:spin organization of $H_2^{16}O$ molecules from solution is probably restricted to the immediate neighborhood of $H_2^{17}O$, and this decoupling in $H_2^{16}O$ molecules is short lived in the bulk solution due to rapid O to P equilibration via proton exchange. This finding is relevant for better understanding of hydration of solutes in the presence of $H_2^{17}O$ and of consequences on chemical reactivity, particularly in proton exchange reactions. This result will help analyze interactions between nuclear spin isomers and the enantio-reactivity of amino acids. $P-$water binds surfaces faster possibly because (unlike O) it can reach the zero-point rotational energy [34],[35] . The electromagnetic interaction between the magnetic moment of a pair of coupled spins and the magnetic moment of a chiral molecule are thought to have higher probability when spin pairs are in the O state [36] . Earlier work indicated that $D - Asn$-$H_2^{17}O$ complexes are more frequent than $L - Asn - H_2^{17}O$ complexes [11] . These results may also help explain $L : D$ $O\&P$-related differences found earlier in amino acids [8],[37] .

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